PATENT ABSTRACTS OF JAPAN

(11)Publication number : 03-179008
(43)Date of publication of application : 05.08.1991

(51)Int.Cl. C08F 20/06
C08F 2/10
C08F 2/38
C08F 8/14
C08F 8/32

(21)Application number : 01-317674
(22)Date of filing : 08.12.1989

(71)Applicant : NIPPON SHOKUBAI KAGAKU KOGYO CO LTD
(72)Inventor : NAGASUNA KINYA
SUMINAGA NORISUKE
KIMURA KAZUMASA
SHIMOMURA TADAO

(54) PRODUCTION OF WATER-ABSORPTIVE RESIN OF EXCELLENT DURABILITY

(57)Abstract:
PURPOSE: To obtain the title resin excellent in the durability and liquid permeability of a swollen gel and showing a high water absorption rate even to physiologic saline by subjecting an aqueous solution containing a water-soluble, ethylenically unsaturated monomer, a crosslinking agent and a water-soluble chain transfer agent each in a specified amount to aqueous solution polymerization.
CONSTITUTION: An aqueous monomer solution of a concentration of from 30wt.% to the saturation concentration containing a water-soluble, ethylenically unsaturated monomer (e.g. acrylic acid/sodium acrylate mixture), 0.005-5mol%, based on this monomer, crosslinking agent (e.g. trimethylolpropane tri-acrylate) and 0.001-1mol%, based on this monomer, water-soluble chain transfer agent (e.g. sodium hypophosphite) is subjected to aqueous solution polymerization.

LEGAL STATUS
[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

Japanese Unexamined Patent Publication
No. 179008/1991 *(Tokukaihei 3-179008)*

A. Relevance of the Above-identified Document

The following is a partial English translation of exemplary portions of non-English language information that may be relevant to the issue of patentability of the claims of the present application.

B. Translation of the Relevant Passages of the Document

See also the attached English Abstract.

1. Title of the invention

PRODUCTION METHOD OF WATER-ABSORBING RESIN EXCELLENT IN DURABILITY

2. Claims

1. A production method of water-absorbing resin (D) excellent in durability, comprising: performing aqueous polymerization using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A).

2. A production method of water-absorbing resin (F) excellent in durability, comprising cross-linking in the vicinity of a surface of water-absorbing resin (D) is cross-linked by a hydrophilic cross-linking agent that is reactive with a functional group contained in water-absorbing resin (D), which water-absorbing resin (D) is produced by aqueous polymerization performed using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A).

3. A production method as set forth one of Claims 1 and 2, wherein water-soluble chain transfer agent (C) is hypophosphite.

4. A production method as set forth in one of Claims 1 and 2, wherein an amount of cross-linking agent (B) to be used is 0.02 mol% to 1 mol% with respect to water-soluble ethylene-based unsaturated monomer (A).

5. A production method as set forth in one of Claims

1 and 2, wherein the concentration of the water-soluble ethylene-based unsaturated monomer (A) aqueous solution is in the range of from 35% by weight to the saturation concentration.

6. A production method as set forth in one of Claims 1 and 2, wherein water-soluble ethylene-based unsaturated monomer (A) contains at least 50% of (i) acrylic acid and (ii) acrylic acid alkali metal salt and/or ammonium acid.

7. A production method as set forth in Claims 1 and 2, wherein the aqueous polymerization is performed using the water-soluble ethylene-based unsaturated monomer (A) aqueous solution in a reactor vessel having a rotation stir blade.

8. A production method as set forth in Claim 7, wherein the reactor vessel has a plurality of rotation stir blades.

9. A production method as set forth in Claim 8, wherein the reactor vessel having the plurality of rotation stir blades is a two-screwed kneader.

10. A production method as set forth in Claim 9,

wherein 0.04 mol% to 0.4 mol% of cross-linking agent (B) is used with respect to water-soluble ethylene-based unsaturated monomer (A).

11. A production method as set forth in Claim 2, wherein, in (i) 0 parts by weight to 20 parts by weight of water and (ii) 0 parts by weight to 20 parts by weight of hydrophilic organic solvent (G), 0.005 parts by weight to 5 parts by weight of at least one type of hydrophilic cross-linking agent (E) selected from compounds (E-1) containing two or more functional groups reactive with a carboxyl group and/or multivalent metal salt (E-2) is mixed and heated at a temperature of 40°C to 250°C with respect to 100 parts by weight of water-absorbing resin (D).

12. A production method as set forth in Claim 11, wherein hydrophilic cross-linking agent (E) is a compound (E-1) or compounds (E-1).

13. A production method as set forth in Claim 12, wherein the compounds (E-1) are one type or more than one type of compound selected from a polyhydroxy alcohol, a multivalent glycidylether compound, a multivalent oxazoline compound, or a multivalent amine compound.

14. A production method as set forth in Claim 11, wherein 0.5 parts by weight to 10 parts by weight of water is used with respect to 100 parts by weight of water-absorbing resin (D).

15. A production method as set forth in Claim 11, wherein 0 parts by weight to 8 parts by weight of hydrophilic organic solvent (G) is used with respect to 100 parts by weight of water-absorbing resin (D).

16. A production method as set forth in Claim 11, wherein the heating is performed at a temperature of 90°C to 220°C.

1. Detailed description of the invention

[Industrially applicable field]

The present invention relates to a production method of a water-absorbing resin excellent in durability. Specifically, the present invention relates to a production method of a water-absorbing resin that: has excellent absorbency; has excellent absorption rate; has excellent durability after having swelled; can form a swelled gel that is less sticky; and has excellent liquid permeability.

Such water-absorbing resin can be produced inexpensively and easily. Furthermore, the water-absorbing resin is excellent in safety and absorption

power. Therefore, the water-absorbing resin can be widely used in sanitary materials (e.g., sanitary napkins, paper diapers), in water supplying agents for agricultural activities, horticultural activities, or greenery, or in any other materials of absorbing products.

[Prior art]

In recent years, a water-absorbing resin that absorbs water of several tens to hundreds times more amount of a weight of the water-absorbing resin has been developed. Such water-absorbing resin has been widely used in various fields including, for example, a field of sanitary materials (e.g., paper diapers, sanitary napkins), a field of agriculture and forestry, and a field of civil engineering.

As a main raw material of the water-absorbing resin, for example the following materials are known: a cross-linked polymer containing partially-neutralized polyacrylic acid (Japanese Unexamined Patent Publication No. 55-84304); a hydrolysate which is a starch-acrylic graft polymer (Japanese Examined Patent Publication No. 49-43395); a saponificated vinyl acetate-acrylic ester copolymer (Japanese Unexamined Patent Publication No. 52-14689); a cross-linked hydrolyzed acrylonitril copolymer or a hydrolyzed acrylamide copolymer (Japanese Examined Patent Publication No. 53-15959); and cross-linked products thereof.

Such water-absorbing resin is demanded to exhibit,

for example, high absorbency and fast absorption rate when contacting with an aqueous liquid, and excellent suction power for absorbing liquid from a material containing the aqueous liquid.

However, depending upon the usage of the water-absorbing resin, especially durability and temporal stability (stability in terms of changes over time) of the swelled gel, in addition to the properties mentioned above, become necessary. For example, in the case where a conventional water-absorbing resin is used in sanitary materials (e.g., paper diapers), there arises a problem in that a swelled gel of the water-absorbing resin having absorbed urine is deteriorated or decomposed as time passes by. Further, in the case where a conventional water-absorbing resin is used for a long period of time in agricultural or horticultural activities, there also arises a problem in that the swelled gel of the water-absorbing resin is deteriorated or decomposed.

Examples of known methods for preventing deterioration and decomposition of the swelled gel of the water-absorbing resin include: a method wherein an oxygen-containing reducing inorganic salt or a radical chain inhibitor is contained a water-absorbing resin (Japanese Unexamined Patent Publications Nos. 63-118375 and 63-152667); a method wherein an oxidant is contained in a water-absorbing resin (Japanese

Unexamined Patent Publication No. 63-153060); or a method wherein a reductant containing sulfur is contained in a water-absorbing resin (Japanese Unexamined Patent Publication No. 63-272349). These methods, however, require to add an additive in order to prevent the water-absorbing resin from deteriorating. From the point of view of safety, it is not preferable to add another additives, considering that the water-absorbing resin is to be used in sanitary materials or the like.

In this connection, a greater amount of cross-linking agent may be used to increase a cross-linking density of the water-absorbing resin so that the strength of the gel is enhanced and therefore the durability is improved. However, if a greater amount of cross-linking agent that is sufficient for the water-absorbing resin to have enough durability is used, the absorbency decreases significantly. As such, currently, water-absorbing resin that is excellent in safety, high in absorbency, and excellent in durability has not been realized, yet.

Further, in the case where the water-absorbing resin is used in, for example, diapers, there arise additional problems of stickiness of the swelled gel and reduction in the liquid permeability, in addition to the problem of durability mentioned above. The water-absorbing resin contains a water-soluble portion (the portion will be referred to as a water-soluble content). Because of the

presence of the water-soluble content, the swelled gel having absorbed water may become sticky. Further, in the case where the water-absorbing resin is used in absorbing products such as diapers, the liquid permeability may be reduced due to the stickiness. Therefore, when additional urine is supplied, the urine may be leaked. Normally, the amount of water-soluble content and the absorbency are in positive correlation. In order to reduce the water-soluble content, the cross-linking density of the water-absorbing resin needs to be increased. Therefore, if the water-absorbing resin has less water-soluble content, the absorbency also becomes lower.

However, it has been publicly known that the more proportion of the cross-linking agent in the water-absorbing resin is, the more improved the durability would be. However, there is a problem in that the absorbency decreases as the amount of cross-linking agent increases. Further, there has been disclosed a technique in which a chain transfer agent is used in production of water-absorbing resins to improve the absorbency (USP4698404). In this case, however, only few increase in the absorbency is observed for human urine, while the absorbency assuredly improves for water and physiological saline.

[Problem to be solved by the invention]

The present invention is in view of the current

situation described above, and has as an object to provide a production method of a water-absorbing resin excellent in durability.

Another object of the present invention is to provide a production method of a water-absorbing resin that (i) exhibits high absorbency with respect to a physiological saline and especially to a human urine, (ii) exhibits excellent durability when used in disposable diapers, (iii) prevents diapers from exuding liquid absorbed therein, (iv) can form a gel that is less sticky, and (v) exhibits excellent liquid permeability.

[Means for solving problem and effect]

In order to solve the above problems, the inventors have diligently researched, and finally found the followings:

(1) By performing aqueous polymerization, using a particular amount of cross-linking agent (B), on a water-soluble ethylene-based unsaturated monomer (A) aqueous solution that has a concentration in a particular range and contains water-soluble chain transfer agent (C), desirable water-absorbing resin (D) whose (i) durability has improved, (ii) can form gel that is less sticky, and (iii) liquid permeability has improved, while maintaining high absorbency, due to reduced molecular weight of the water-soluble content can be produced with good productivity.

(2) Further, by cross-linking, using hydrophilic cross-linking agent (E), the vicinity of the surface of the water-absorbing resin (D) produced by production method (1) described above, water-absorbing resin (F) that exhibits (a) better water absorbency, (b) better durability, (c) less gel stickiness, (d) better liquid permeability, and (e) better water absorption property, while maintaining high absorbency, can be produced.

In other words, the present invention relates to:

a production method of a water-absorbing resin (D) excellent in durability, which method is adapted so that the method includes performing aqueous polymerization using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to and monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A); and

a production method of a water-absorbing resin (D) excellent in durability, which method is adapted so that the method includes performing cross-linking in the vicinity of a surface of water-absorbing resin (D) is cross-linked by a hydrophilic cross-linking agent that is reactive with a functional group contained in

water-absorbing resin (D), which water-absorbing resin (D) is produced by aqueous polymerization performed using a monomer (A) aqueous solution that has a concentration in the range of from 30% by weight to a saturation concentration and contains (i) water-soluble ethylene-based unsaturated monomer (A), (ii) 0.005 mol% to 5 mol% of cross-linking agent (B) with respect to and monomer (A), and (iii) 0.001 mol% to 1 mol% of water-soluble chain transfer agent (C) with respect to monomer (A).

The following specifically describes the present invention.

Water-soluble ethylene-based unsaturated monomer (A) (the monomer will be referred to as monomer (A)) of the present invention contains a functional group. Examples of monomer (A) include acrylic acid, methacrylic acid, maleic acid, fumaric acid, crotonic acid, itaconic acid, vinylbenzenesulfonic acid, 2-(meth)acrylamide-2-methylpropanesulfonic acid, 2-(meth)acryloylethanesulfonic acid, 2-(meth)acryloylpropanesulfonic acid, and their alkali metal salts and ammonium salts; and acrylamide, methacrylamide, 2-hydroxyethyl(meth)acrylate, methoxypolyethyleneglycol(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminopropyl(meth)acrylate,

N,N-diethylaminopropyl(meth)acrylamide, and their quaternary salts. At least one of the above may be selected and used.

In view of properties and costs of water-absorbing resin that is produced, it is preferable that acrylic acid, among monomers (A) listed above, be used as a main content. In this case, acrylic acid and its alkali metal salt and/or ammonium salt is contained, preferably, at a percentage of 50% by weight or greater, and more preferably, at a percentage of 75% by weight or greater with respect to monomer (A).

Further, in order to produce a water-absorbing resin excellent in durability, in the present invention, it is necessary to use a particular amount of cross-linking agent (B) that contains two or more polymerizable unsaturated groups and/or a reactive functional group per molecule. As cross-linking agent (B), for example a compound containing two or more polymerizable unsaturated group per molecule may be used. Examples thereof include N,N'-methylenebisacrylamide, (poly)ethyleneglycoldi(meth)acrylate, (poly)propyleneglycoldi(meth)acrylate, glycerictri(meth)acrylate, glycericacrylatemethacrylate, multivalent metal salts of (meth)acrylic acid, trimethylolpropanetri(meth)acrylate, triallylamine, triallylcyanurate, triallylisocyanurate, and

triallylphosphate and the like. Further, examples of cross-linking agent (B) containing reactive functional groups in the case where monomer (A) contains a carboxyl group include: polyhydric alcohols such as ethylene glycol; diethylene glycol, triethylene glycol, polyethyleneglycol, propylene glycol, dipropylene glycol, polypropylene glycol, and glycerin; multivalent glycidyl compounds such as (poly)ethylene glycoldiglycidylether, and glycerolpolyglycidylether; multivalent amines such as ethylenediamine, and polyethyleneimine; multivalent isocyanate compounds; multivalent metal salts and the like. Further, examples of cross-linking agent (B) containing both a polymerizable unsaturated group and a reactive functional group per molecule include glycidyl(meth)acrylate and N-methylol(meth)acrylamide. From the points of view of durability and water absorbency of the water-absorbing resin that is produced, it is especially preferable to use at least one of the compounds containing more than one polymerizable unsaturated groups in a molecular, among the cross-linking agents (B).

The amount of cross-linking agent (B) to be used in the present invention is 2 to 10 times greater in mol, or more preferably 4 to 10 times greater in mol than the amount of the cross-linking agent used in the case where the polymerization is performed under the same

conditions, except that water-soluble chain transfer agent (C) is not used to obtain a target water-absorbency. Specifically, the amount of cross-linking agent (B) to be used is 0.005 mol% to 5 mol% with respect to monomer (A). If less than 0.005 mol% of cross-linking agent (B) is used, a water-absorbing resin with high absorbency is produced. However, the water-absorbing resin is inferior in durability, contains many water-soluble contents, and has a higher molecular weight. This causes the gel of the water-absorbing resin to be stickier, and the liquid permeability to be degraded. On the other hand, if more than 5 mol% of cross-linking agent (B) is used, the absorbency becomes extremely low. Further, it is preferable that the amount of cross-linking agent to be used be in the range of from 0.02 mol% to 1 mol%, more preferably in the range of from 0.04 mol% to 0.4 mol%, and even more preferably in the range of from 0.08 mol% to 0.2 mol%, although it depends upon the amount of water-soluble chain transfer agent (C) to be used. The amount of water-soluble chain transfer agent (C) will be described later.

Further, in addition to the above method utilizing cross-linking agent (B), a method in which graft polymerization is performed to form a cross-link may be carried out simultaneously. For example, the monomer (A) aqueous solution may be polymerized in the presence of a

hydrophilic polymer (e.g., cellulose, starch, polyvinyl alcohol), so that a cross-link is formed as a result of the graft polymerization. It is preferable that the water-soluble macromolecule be used in the range of from 1% by weight to 50% by weight with respect to monomer (A).

In the present invention, it is necessary to use a particular amount of water-soluble chain transfer agent (C).

According to the present invention, (i) a particular amount of water-soluble chain transfer agent (C) is selected, and (ii) a large amount of cross-linking agent is used in polymerization to form a high cross-link, which amount is 2 to 100 greater in mol than that used in an ordinary production method. With such an arrangement, the present invention provides an excellent water-absorbing resin that (i) is highly excellent in durability, (ii) exhibits high absorbency not only to physiological saline but also to human urine, (iii) provides less negative influence (e.g., stickiness of gel, decrease in the liquid permeability) due to low molecular weight of the water-soluble content can be produced.

The water-soluble chain transfer agent (C) for use in the present invention is not particularly limited, provided that water-soluble chain transfer agent (C) is soluble in water or in a water-soluble ethylene-based unsaturated

monomer. The water-soluble chain transfer agent (C) may be a thiol, a thiol acid, a secondary alcohol, an amine, a hypophosphite, or the like. Specific examples of the water-soluble chain transfer agent (C) include: mercaptoethanol, mercaptopropanol, dodecyl mercaptan, thioglycolic acid, thiomalic acid, 3-mercaptopropionic acid, isopropanol, sodium hypophosfite, formic acid, and their salts. One of, or two or more of the water-soluble chain transfer agents (C) are selected and used. Because of their effect, it is preferable that the water-soluble chain transfer agent (C) be hypophosphite such as sodium hypophosfite.

An amount of the water-soluble transfer agent (C) to add is, with respect to monomer (A), in the range of from 0.001 mol% to 1 mol%, preferably in the range of from 0.005 mol% to 0.3 mol%, even though it depends on the type and amount of internal cross-linking agent (B) and the concentration of monomer (A) aqueous solution. In the case where the amount is less than 0.001 mol%, the amount of cross-linking agent (B) to be used in the present invention is not preferable because the cross-linking density would become high and the absorbency would become too low. Further, it is not preferable to use more than 1 mol% of cross-linking agent (B) because the water-soluble content would increase and the durability would decrease.

The concentration of monomer (A) aqueous solution used in the present invention is in the range of from 30% by weight to the saturation concentration. It is more preferable that the concentration be in the range of from 35% by weight to the saturation concentration. If the concentration is below 30% by weight, the productivity per unit-reaction-volume decreases. Moreover, the drying step takes longer time, and therefore the productivity decreases. Therefore, from industrial view, the concentration below 30% by weight is not preferable. In conventional polymerization methods, if the polymerization is performed at a concentration close to the saturation concentration in order to improve the productivity, unnecessary reactions such as self-cross-linking occur, and the absorbency is decreased. Therefore, the amount of cross-linking agent (B) that can be used in the polymerization is limited, and thus only a water-absorbing resin having poor durability is produced. However, with the method of the present invention, self-cross-linking reaction is prevented by choosing the amount of water-soluble chain transfer agent (C) to be used. This makes it possible to increase the amount of cross-linking agent (B) to be used, and therefore a water-absorbing resin that is excellent in durability and has high absorbency can be produced at a high concentration at good productivity.

Further, if necessary, a thickener may be used in the monomer (A) aqueous solution. Examples of the thickener include: polyvinylpyrrolidone; polyacrylamide; methyl cellulose; and hydroxyethyl cellulose and the like.

In the present invention, among publicly-known polymerization techniques (e.g., aqueous polymerization, reverse-phased suspension polymerization, precipitate polymerization, bulk polymerization, polymerization by activation energy such as ultraviolet ray or electron ray), aqueous polymerization is employed for polymerizing using the monomer (A) aqueous solution to produce a water-absorbing resin that has excellent properties and productivity, and requires less costs. Exemplary methods of aqueous polymerization include: casting polymerization performed in a cast (Japanese Examined Patent Publication No. 48-42466 (Tokukosho 48-42466)); polymerization performed using a belt conveyer (Japanese Unexamined Patent Publication No. 58-49714 (Tokukaisho 58-49714)); and polymerization performed in, for example, a kneader having a stir blade that can comminute hydrate gel polymers (Japanese Unexamined Patent Publication No. 57-34101 (Tokukaisho 57-34101)).

In performing the aqueous polymerization, it is preferable that (i) chain transfer reaction take place uniformly with water-soluble chain transfer agent (C) and (ii) the cross-linking reaction occurs uniformly with

cross-linking agent (B). In order to produce a water-absorbing resin having better properties, it is preferable that the heat generated during the polymerization be removed uniformly. In order to do so, it is preferable that, instead of the polymerization method in which the polymerized gel is kept as one united body, the polymerized gel of the reaction system be stirred from the beginning to the end of the polymerization, or sometimes during the polymerization or throughout the polymerization so that the heat generated during the polymerization be removed uniformly, instead of a polymerization method in which the polymerized gel is unified. It is thus preferable that the polymerization reaction be performed in a reactor vessel having a rotation stir blade. The reactor vessel having a rotation stir blade is not particularly limited, but a reactor vessel that can stir the polymerized gel with greater power is preferable. An exemplary reactor vessel is a vessel that shears the polymerized gel by the rotation stir blade, which polymerized gel is generated as the polymerization proceeds. Further, in order to increase the stirring power, it is preferable that a plurality of rotation stir blades be provided. Examples of the reactor vessel include a single-screwed mix-kneader, a single-screwed extruder, a two-screwed kneader, and a three-screwed kneader. Further, by using the two-screwed kneader, polymerized

gel can be fragmented and stirred evenly throughout the polymerization, and the heat generated during the polymerization can be removed uniformly. As a result, a water-absorbing resin having excellent properties can be produced. Therefore, it is preferable to use a two-screwed kneader.

In the present invention, the radical polymerization initiator to be used in the aqueous polymerization is not particularly limited, as long as the radical polymerization initiator is water-soluble. For example, the followings may be used as the radical polymerization initiator: persulfates such as potassium persulfate, ammonium persulfate, sodium persulfate and the like; hydroperoxides such as hydrogen peroxide, t-butylhydroperoxide, cumenehydroperoxide and the like; azo compounds such as 2,2'-azobis(2-amizinopropane)dihydrochloride) and the like; secondary cerium salt, permanganate, and the like. In view of, for example, (i) properties of the water-absorbing resin to be produced and (ii) safety of decomposition products, it is preferable that the radical polymerization initiator be one or more of persulfate, hydroperoxide, and azo compounds.

Further, in the case where the radical polymerization initiator is an oxidizing radical polymerization initiator, reductants may be combined to be used as a redox type initiator. Examples of the reductants include: sulfites

(hydrogen salt) such as sodium sulfite, sodium hydrogen sulfite and the like; thisulfate such as sodium thiosulfate and the like; dithionite; metal salt such as copper sulfate, iron sulfate and the like; organic reductants such as b-ascorbic acid and the like; aniline; and amines such as monoethanolamine and the like.

Although a wide range of the amount of the radical polymerization initiator may be used, normally it is preferable that the range of the amount of the radical polymerization initiator be 0.001 mol% to 2 mol% with respect to monomer (A), or more preferably 0.01 mol% to 0.5 mol% with respect to monomer (A). If less than 0.001 mol% of radical polymerization initiator is used, the induction period becomes longer and the amount of the residual monomer easily increases. Further, in a conventional polymerization method, if the amount of the polymerization initiator is increased in order to (a) reduce the amount of the residual monomers or (b) shorten the induction period and the polymerization period, unnecessary reactions such as self-cross-linking may occur, thereby degrading the absorbency. Thus, the amount of initiator has been limited. On the contrary, with the present invention, these disadvantages are solved, and the water-absorbing resin having excellent properties is produced even when the amount of initiator is increased. If, however, more than 2 mol% of radical polymerization

initiator is used, not only expected effects from the increased amount cannot be achieved, but also it becomes difficult to control the polymerization reaction. Accordingly, it is not preferable to use more than 2 mol% of radical polymerization initiator.

The water-absorbing resin produced by the present invention may be polymerized at high concentration, and the water-absorbing resin may be dried with the heat generated during the polymerization while being polymerized. Depending upon the proportion of water contained after performance of the polymerization, the hydrate gel produced may be dried further and then used in the water-absorbing resin. For the drying, publicly-known drying methods may be employed. Exemplary methods thereof include: azeotropy dehydration in an organic solvent; drying with a mechanical draft oven; drying with a reduced-pressure dryer; drying with a microwave dryer; drying with an infrared dryer; and drying with a belt having heated to a predetermined temperature or a drum dryer having heated to a predetermined temperature. It is preferable that the polymerized hydrate gel be dried by one of the above methods at 80°C or above. It is more preferable that the hydrate gel be dried at 80°C to 230°C. In view of productivity, it is not preferable to dry the hydrate gel at a temperature below 80°C because it consumes too much

time. Careful attention is required in drying the hydrate gel at 230°C or above because the water-absorbing resin may be deteriorated at such high temperature.

Further, the water-absorbing resin produced by the polymerization and the drying is pulverized and/or classified, if necessary, before being used.

Further, the present invention also provides a production method of water-absorbing resin (F). In the production method, the water-absorbing resin (F) is produced by cross-linking, with particular hydrophilic cross-linking agent (E), in the vicinity of the surface of water-absorbing resin (D) produced by the production method described above. Water-absorbing resin (D) produced by the production method of the present invention has significantly improved water absorbency, compared with conventional water-absorbing resins. Further, water-absorbing resin (F), on which cross-linking was performed in the vicinity of the surface, has better durability and water absorbency than water-absorbing resin (D), on which cross-linking has not been performed in the vicinity of the surface.

Hydrophilic cross-linking agent (E) used in the present invention is compound (E-1) containing more than one functional group per molecule and/or multivalent metal salt (E-2) containing more than one functional group per molecule, which functional group is reactive

with a carboxyl group. Examples of compounds (E-1) in the case where water-absorbing resin (D) contains a carboxyl group include: polyhydroxy alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethyleneglycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, propylene glycol, glycerin, polyglycerin, trimethylolpropane, pentaerythritol, sorbitol, polyvinyl alcohol and the like; ethylene glycoldiglycidylether; multivalent glycidylether compounds such as ethyleneglycoldiglycidylether, polyethyleneglycoldiglycidylether, glycerolpolyglycidylether, diglycerolpolyglycidylether, polyglycerolpolyglycidylether, propylene glycoldiglydiglycidylether, polypropylene glycoldiglycidylether and the like; multivalent amine compounds such as ethylenediamine, diethylenetriamine, triethylenetetramine, polyethyleneimine and the like; multivalent oxazoline compounds such as 1,2-ethylenebisoxazoline, polyisopropenyloxazoline and the like; haloepoxy compounds such as epichlorohydrin and the like; multivalent aziridine compounds; and multivalent isocyanate compounds; and the like. Examples of multivalent metal salt (E-2) in the case where water-absorbing resin (D) contains a carboxyl group include: hydroxide of zinc, hydroxide of calcium, hydroxide of magnesium, hydroxide of aluminum,

hydroxide of iron, hydroxide of zirconium, chloride of zinc, chloride of calcium, chloride of magnesium, chloride of aluminum, chloride of iron, and chloride of zirconium, and the like. It is preferable that one kind or more than one kind of the above be used. It is preferable to use compound (E-1) as an essential component. In view of surface cross-linking effects, it is especially preferable that a polyhydric alcohol, a multivalent glycidyl compound, or a multivalent amine be used as hydrophilic cross-linking agent (E). Further, a combination of compound (E-1) and multivalent metal salt (E-2) may be used as hydrophilic cross-linking agent (E) to improve combined properties.

The amount of hydrophilic cross-linking agent (E) used in the present invention is 0.005 parts by weight to 5 parts by weight with respect to 100 parts by weight of water-absorbing resin (D) produced by the production method described above. It is preferable that the amount be in the range of from 0.01 parts by weight to 1 part by weight with respect to 100 parts by weight of water-absorbing resin (D) produced by the production method described above. If the amount is within this range, water-absorbing resin (F) having excellent properties and cross-linked surface can be produced. If more than 5 parts by weight of hydrophilic cross-linking agent (E) is used, it is not only uneconomical, but also

may cause unreacted hydrophilic cross-linking agent (E) to remain in water-absorbing resin (F) that has been produced. Moreover, this amount of hydrophilic cross-linking agent (E) is excess for achieving desired cross-linking effects, reducing the water absorbency of water-absorbing resin (F) that is produced. Therefore, it is not preferable to use more than 5 parts by weight of hydrophilic cross-linking agent (E). Further, in the case where less than 0.005 parts by weight of hydrophilic cross-linking agent (E) is used, it is difficult to achieve the effects of the present invention.

In the present invention, water and/or hydrophilic organic solvent (G) may be used in mixing water-absorbing resin (D) and hydrophilic cross-linking agent (E).

In the present invention, the amount of water to be used is 0 part to 20 parts by weight with respect to 100 parts by weight of water-absorbing resin (D). It is preferable that the amount be in the range of from 0.5 parts by weight to 10 parts by weight.

Examples of hydrophilic organic solvent (G) include: lower alcohols such as methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, t-butanol and the like; ketones such as acetone, methylethylketone, methylbutylketone and the like; ethers such as dioxane tetrahydrofuran and the like; amides such as N,N-dimethylformamide and the like; and sulfoxides such

as dimethylsulfoxide and the like. The amount of water-absorbing resin (D) to be used is in the range of from 0 parts by weight to 20 parts by weight with respect to 100 parts by weight of water-absorbing resin (D). It is preferable that the amount be in the range of from 0 parts by weight to 8 parts by weight.

The followings are exemplary methods, according to the present invention, of (i) mixing water-absorbing resin (D) and hydrophilic cross-linking agent (E) and (ii) cross-linking in the vicinity of the surface of the water-absorbing resin:

(i) Hydrophilic cross-linking agent (E) and, if necessary, a mixed solution of water (water vapor) and/or hydrophilic organic solvent (G) may be added to water-absorbing resin (D) by spraying or dropping;

(ii) Water-absorbing resin (D) is dispersed and suspended in a hydrophobic organic solvent that is inactive in polymerization, and hydrophilic cross-linking agent (E) and, if necessary, water and/or hydrophilic organic solvent (G) are added while being stirred; and

(iii) water-absorbing resin (D) is dispersed in a mixed solvent of water and hydrophilic organic solvent (G), and hydrophilic cross-linking agent (E) is added.

In case (ii), it is preferable that hydrophilic cross-linking agent (E) be emulsified, using a particular surfactant, into a hydrophobic organic solvent and be

suspended in advance, and then the emulsified solution be added to a solution in which water-absorbing resin (D) has been dispersed and suspended.

As described above, an ordinary heating machine or heating oven may be used to perform a heating treatment on a mixture of (i) water-absorbing resin (D) produced by the method of the present invention, (ii) hydrophilic cross-linking agent (E), and, if necessary, water and/or hydrophilic organic solvent (G). Examples of the heating machine and the heating oven include: a trench type mixing dryer; a rotary type dryer; a disk type dryer; a kneading dryer; a fluidized bed type dryer; an air-flow type dryer; an infrared dryer; a dielectric heating dryer; and the like. Further, hydrophilic cross-linking agent (E) may be added, in an organic solvent, to water-absorbing resin (D) by method (ii), and thereafter heated to react in the organic solvent.

It is preferable that the heat treatment be performed at the heating treatment in the range of from 40°C to 250°C, more preferably in the range of from 90°C to 220°C, although it depends upon which kind of hydrophilic cross-linking agent (E) is used. If the heating treatment is performed at a temperature below 40°C, not only it takes time to react and therefore the productivity decreases, but also a part of hydrophilic cross-linking agent (E) may not react and may remain in water-absorbing resin (F) that is

produced. Therefore, it is not preferable that the heating treatment be performed at a temperature below 40°C. On the other hand, if the heating treatment is performed at a temperature above 250°C, deterioration by the heat may occur in some kinds of water-absorbing resin (D). Therefore, careful attention is required.

Note that water-absorbing resin (F) whose surface is cross-linked or water-absorbing resin (D) whose surface is not cross-linked may be pulverized and agglomerated, if necessary.

[Effect of the invention]

The water-absorbing resin produced by the method of the present invention has the following advantages, which could not be achieved by the conventional methods: excellent durability of swelled gel; high absorbency with respect to physiological saline and especially to human urine; low molecular weight of the water-soluble content; significantly reduced stickiness of swelled gel; significantly improved liquid permeability; and excellent safety. According to the method of the present invention, such excellent water-absorbing resin can be easily produced by performing aqueous polymerization, in the presence of a particular amount of cross-linking agent (B) and a particular amount of water-soluble chain transfer agent (C), on water-soluble ethylene-based unsaturated monomer (A). Furthermore, by cross-linking, using

particular hydrophilic cross-linking agent (E), in the vicinity of the surface of water-absorbing resin (D) that has been produced, water-absorbing resin (F) having significantly improved absorption rate and durability can be produced. Water-absorbing resin (D) and water-absorbing resin (F) that have excellent water absorbency can be produced inexpensively. This could not be achieved by a conventional water-absorbing resin. Therefore, water-absorbing resin (D) and water-absorbing resin (F) may be widely used in various fields including sanitary material, foods, civil engineering, agriculture.

As described above, the water-absorbing resin produced by the production method of the present invention has the following advantages.

(1) The swelled gel has excellent durability because, in the present invention, the high absorbency is maintained even when a large amount of cross-linking agent is used. In contrast, conventional swelled gels have had poor durability because polymerization is performed using a reduced amount of cross-linking agent in order to produce a water-absorbing resin having high absorbency.

(2) The absorbency with respect to human urine is high. This could not be achieved by the conventional water-absorbing resins.

(3) The water-absorbing resins can be produced at high productivity because even when the monomer is

polymerized at a high concentration close to the saturation concentration, a water-absorbing resin having excellent properties can be produced without causing unnecessary reactions such as self-cross-linking. Therefore, the polymerization can be performed at a high concentration.

(4) The water-absorbing resin of the present invention has high absorbency, and the water-soluble content associated therewith does not provide negative influences (e.g., stickiness of swelled gel due to water-soluble content, reduction in the liquid permeability) because the molecular weight of the water-soluble content is small.

(5) By performing the cross-linking in the vicinity of the surface, (i) the water absorbency can be better than the absorbency achieved by a conventional surface cross-linking of water-absorbing resin, and (ii) the durability and the absorption rate can be improved.

(6) A small amount of residual monomer is used, because high absorbency can be achieved even when an increased amount of polymerization initiator is used. In contrast, conventionally, if the amount of polymerization initiator is increased in order to reduce the residual monomer or shorten the induction period and polymerization period, unnecessary reaction such as self-cross-linking is generated. Therefore, high absorbency

could not be achieved.

(Examples)

The following describes the present invention, with reference to Examples. The scope of the present invention, however, is not limited to the Examples. Note that the properties of the water-absorbing resin in the Examples indicate the values measured by the testing methods described later. Further, the term “part(s)” means “part(s) by weight”.

(1) Absorbency of physiological saline

In a beaker containing 150 ml of 0.9% by weight sodium chloride aqueous solution, 1.0 g of water-absorbing resin was soaked and stirred slowly using a magnetic stirrer. After six hours had passed, the swelled gel was filtered by a wire net, and the weight of the swelled gel from which water had been removed adequately was measured. Then, the absorbency was calculated using the formula below.

absorbency(g/g) = weight of swelled gel/weight of water-absorbing resin

(2) Absorbency of human urine

The absorbency of human urine was measured under the same conditions, except that sample human urine of 10 adult males were used instead of the physiological

saline used in the case (1).

(3) Water-soluble content

In 1000 ml of deionized water, 0.5 g of water-absorbing resin was dispersed. After 12 hours had passed, this was filtered by a paper filter, and the solid content in the filtrate was measured. Then, the water-soluble content was calculated using the formula below.

$$\text{water-soluble content (\%)} = \frac{\text{weight of filtrate (g) x solid content in filtrate (\%)}}{0.5\ \text{g}}$$

(4) Molecular weight of water-soluble content

By using, as standard, various polysodium acrylic acids whose molecular weights had already been calculated, the molecular weight of the water-soluble content obtained in item (3) was worked out by using gel permeation chromatography.

(5) Tolerance of swelled gel

A commercially-available diaper for children (weight: 72 g) formed of nonwoven fabric, cotton-like pulp, water-absorbing paper, and water-proof film is cut into a half, and 2.5 g of polymer was evenly dispersed between the cotton-like pulp and the water-absorbing paper, and 120 ml of adult human urine was added. Then, the diaper

was left at 37°C. Thereafter, the diaper was opened to observe the state of the swelled gel after (i) 6 hours, (ii) 12 hours, and (iii) 18 hours. The degree of deterioration was evaluated using three categories: good, average, and poor.

Good	: shape of swelled gel is maintained
Average	: shape of swelled gel is partially collapsed
Poor	: shape of swelled gel is collapsed, and the swelled gel is muddy

(6) Amount of exudation of absorbed liquid

On the nonwoven fabric of the diapers for children after 18 hours, which diapers had been used in the examination of durability of the swelled gel, 10 sheets of 23-by-23-cm paper towels folded into two were overlaid. Then, a pressure of 40 g/cm^2 was applied for one minute. Thereafter, the amount of urine returned to the paper towels was measured.

(7) Stickiness of swelled gel

The stickiness (feeling of dryness) of the swelled gel whose absorbency had been calculated in (1) was determined by hand-touching. The feeling of dryness was evaluated using three categories: good, average, and poor.

Good	: swelled gel is very dry, providing feeling of dryness

Average : swelled gel is partially sticky

Poor : swelled gel is sticky, and hand becomes slimy

(8) Liquid permeability of swelled gel

As illustrated in Figure 1, in a plate 1 having an inner diameter of 53 mm, 1.0 g of water-absorbing resin was placed and 10 ml of human urine was poured therein, thereby obtaining swelled gel 2. On the swelled gel 2, a paper towel 3 having a diameter of 53 mm was placed. Further, a test tube 4 made of acrylic resin, provided with a protruding cylinder, and having doughnut-shaped was placed at the center thereof, as illustrated in Figure 1. After this was left at a room temperature for one hour, 6 ml of human urine was poured from the inlet opening 5.. The time taken for all of the human urine to be absorbed into the polymer was measured. The measured time is used as a parameter of the liquid permeability of the swelled gel.

(Example 1)

A monomer aqueous solution with the concentration of 37% and the neutralization ratio of 75% was produced using (i) 4380 g of 37% by weight aqueous solution containing 414 g of acrylic acid and sodium acrylic acid, (ii) 6.815 g (0.1 mol% with respect to monomer (A)) of trimethylolpropanetriacrylate, which functions as

cross-linking agent (B), (iii) 0.195 g (0.008 mol% with respect to monomer (A)) of sodium hypophosfite1hydrate, which functions as water-soluble chain transfer agent (C), and (iv) 670 g of ion-exchange water. Thereafter, nitrogen gas was blown to expel dissolved oxygen.

In a reactor vessel having a lid and a twin-arm type kneader (content volume of 10 liters) made of stainless-steel and having a jacket and two sigma blades, a monomer (A) aqueous solution was supplied and nitrogen gas was blown to fill a reaction system with nitrogen. Thereafter, the two sigma blades were rotated, while hot water of 35°C was streamed in the jacket to heat, 2.62 g of ammonium persulfate and 0.12 g of sodium hydrogen sulfite, both of which function as polymerization initiators, were added to start polymerization. At a peak of polymerization, hydrate gel polymer was fragmented to have a diameter of approximately 5 mm. Then, the stirring was continued, and 60 minutes after the beginning of the polymerization, the lid was moved to take out the gel. The fine particles of hydrate gel polymer that had been produced were (i) dispersed over a wire net having 50 meshes and (ii) dried with hot air of 170°C for 50 minutes. Then, the dried hydrate gel polymer was pulverized with a hammer type pulverizer, and filtered by a wire metal having 20 meshes. As a result, water-absorbing resin (1) that had filtered through the wire net having 20 meshes

was produced.

The properties of water-absorbing resin (1) were evaluated, and results of the evaluation are shown in Table 1.

(Example 2)

The same operations as in Example 1 were performed, except that 1.219 g (0.05 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) sodium hypophosfite1hydrate was used. As a result, water-absorbing resin (2) was produced.

The properties of water-absorbing resin (2) were evaluated, and results of the evaluation are shown in Table 1.

(Example 3)

The same operations as in Example 1 were performed, except that (i) 21.988 g (0.2 mol% with respect to monomer) of polyethyleneglycoldiacrylate (n=8) was used as cross-linking agent (B), and (ii) 2.44 g (0.1 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) sodium hypophosfite1hydrate was used. As a result, water-absorbing resin (3) was produced.

The properties of water-absorbing resin (3) were evaluated, and results of the evaluation are shown in Table 1.

(Example 4)

The same operations as in Example 1 were performed,

except that (i) 54.97 g (0.5 mol% with respect to monomer) of cross-linking agent (B) polyethyleneglycoldiacrylate(n=8) was used, and (ii) 9.76 g (0.4 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) sodium hypophosfite1hydrate was used. As a result, water-absorbing resin (4) was produced.

The properties of water-absorbing resin (4) were evaluated, and results of the evaluation are shown in Table 1.

(Example 5)

The same operations as in Example 1 were performed, except that (i) 2.152 g of N,N'-methylenebisacrylamide (0.06 mol% with respect to monomer (A)) was used in place of cross-linking agent (B), and (ii) 3.45 g of thiomalic acid (0.1 mol% with respect to monomer) was used in place of water-soluble chain transfer agent (C). As a result, water-absorbing resin (5) was produced.

The properties of water-absorbing resin (5) were evaluated, and results of the evaluation are shown in Table 1.

(Example 6)

The same operations as in Example 1 were performed, except that (i) the amount of ion-exchange water to be used was changed to 50 g, (ii) the monomer (A) aqueous solution with the concentration of 42% was used, (iii) 17.07 g (0.1 mol% with respect to monomer (A)) of

polyethyleneglycoldiacrylate(n=14) was used as cross-linking agent (B), and (iv) 0.69 g (0.02 mol% with respect to monomer (A)) of water-soluble chain transfer agent (C) thiomalic acid was used. As a result, water-absorbing resin (6) was produced.

The properties of water-absorbing resin (6) were evaluated, and results of the evaluation are shown in Table 1.

(Example 7)

Forty grams of corn starch and 600 g of ion-exchange water were placed in a reactor vessel provided with a stir-stick, a nitrogen gas blow tube, and a thermometer, stirred for one hour at 55°C, and thereafter cooled down to 30°C. To the starch aqueous solution, (i) 300 g of acrylic acid, (ii) 1.92 g (0.3 mol% with respect to monomer (A)) of N,N'-methylenebisacrylamide, which functions as cross-linking agent (B), (iii) 0.94 g (0.15 mol% with respect to monomer (A)) of thiomalic acid, which functions as water-soluble chain transfer agent (C), were solved.

As a result, a monomer aqueous solution with the concentration of 33% and the neutralization ratio of 0% was produced.

The monomer aqueous solution was adjusted to 35°C, and 0.20 g of sodium persulfate, which functions as the polymerization initiator, and 0.04 g of l-ascorbic acid were added and then stirred for three hours to be polymerized.

To a hydrate gel polymer, 389 g of 30% by weight caustic soda aqueous solution was added so that the neutralization ratio is adjusted to 70%. Then, it was dried and pulverized in the same manner as in Example 1. As a result, water-absorbing resin (7) was produced.

The properties of water-absorbing resin (7) were evaluated, and results of the evaluation are shown in Table 1.

(Example 8)

To 72 g of acrylic acid, 22.2 g of deionized water was added. A mixture produced thereby was used as a neutralizer, and (i) 49.5 g of potassium hydroxide with the purity of 85%, (ii) 0.1 g (0.065 mol% with respect to monomer (A)) of N,N'-methylenebisacrylamide, which functions as cross-linking agent (B), 0.225 g (0.15 mol% with respect to monomer (A)) of thiomalic acid, which functions as water-soluble chain transfer agent (C), were added sequentially. As a result, a monomer aqueous solution with the concentration of 70% and the neutralization ratio of 75% was produced.

This monomer aqueous solution was kept at 70°C in a nitrogen air stream with a thickness of approximately 5 mm. Then, 0.1 g of ammonium persulfate and 0.02 g of sodium hydrogen sulfite were added, and polymerization was performed. The polymerization started immediately. After 10 minutes had passed, a polymerized gel that was

almost dried was taken out, dried, and pulverized, in the same manner as in Example 1. As a result, water-absorbing resin (8) was produced.

The properties of water-absorbing resin (8) were evaluated, and results of the evaluation are shown in Table 1.

(Example 9)

To 100 parts of water-absorbing resin (5) that had been produced in Example 1, 0.1 part of ethylene glycoldiglycidylether, five parts of water, and one part of isopropyl alcohol were added. Thereafter, a mixture produced thereby was treated, in a dryer, with heat at 100°C for 30 minutes. As a result, water-absorbing resin (9) was produced.

Water-absorbing resin (9) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Example 10)

To 100 parts of water-absorbing resin (2) that had been produced in Example 2, one part of glycerin, six parts of water, and one part of acetone were added. Thereafter, the mixture was (i) putted into a blender whose jacket had been heated to 230°C by a heating medium, (ii) mixed, and (ii) treated with heat. As a result, water-absorbing resin (10) was produced.

Water-absorbing resin (10) that had been produced

in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Example 11)

To 100 parts of water-absorbing resin (3) that had been produced in Example 3, a solution composed of (i) 0.1 parts of ethyleneglycidylether, 3 parts of water, and 6 parts of methanol were added. A mixture produced thereby was treated, in a dryer, with heat at 130°C for one hour. As a result, water-absorbing resin (12) was produced.

Water-absorbing resin (11) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Example 12)

To 100 parts of water-absorbing resin (4) that had been produced in Example 4, 10 parts of aqueous solution composed of (i) one part of aluminium sulfate, (ii) one part of glycerin, and (iii) 8 parts of water were added. A mixture produced thereby was treated with heat at 200°C for 30 minutes. As a result, water-absorbing resin (12) was produced.

Water-absorbing resin (12) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 1)

The same operations as in Example 7 were performed, except that 0.273 g of cross-linking agent (B) (0.004 mol%

with respect to monomer (A)) was used. As a result, comparative water-absorbing resin (1) was produced.

Comparative water-absorbing resin (1) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 2)

The same operations as in Example 7 were performed, except that water-soluble chain transfer agent (C) sodium hypophosfite1hydrate was not added. As a result, comparative water-absorbing resin (2) was produced.

Comparative water-absorbing resin (2) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 3)

The same operations as in Example 1 were performed, except that (i) water-soluble chain transfer agent (C) sodium hypophosfite1hydrate was not added and (ii) 3.41 g of cross-linking agent (B) (0.05 mol% with respect to monomer (A)) was used. As a result, comparative water-absorbing resin (3) was produced.

Comparative water-absorbing resin (3) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 4)

The same operations as in Example 1 were performed, except that (i) water-soluble chain transfer agent (C)

sodium hypophosfite1hydrate was not added and (ii) cross-linking agent (B) was replaced by 17.73 g of N,N'-methylenebisacrylamide (0.5 mol% with respect to monomer (A)). As a result, comparative water-absorbing resin (4) was produced.

Comparative water-absorbing resin (4) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Example 5)

The same operations as in Example 7 were performed, except that cross-linking agent (B) was not added. As a result, comparative water-absorbing resin (5) was produced.

Comparative water-absorbing resin (5) that had been produced in the manner described above was analyzed, and results of the analysis are shown in Table 1.

(Comparative Examples 6 to 8)

The same operations as in Example 9 were performed using comparative water-absorbing resins (1) to (3) that had been produced in Comparative Examples 1 to 3, respectively. As a result, comparative water-absorbing resins (6) to (8) were produced.

Comparative water-absorbing resins (6) to (8) that had been produced in the manner described above were analyzed, and results of the analysis are shown in Table 1.

4. Brief description of drawings

Figure 1 illustrates a test equipment for testing the liquid permeability of a swelled gel.

1 ...... plate

2 ...... swelled gel

3 ...... paper towel

4 ...... test vessel made of acrylic resin

5 ...... inlet opening

Applicant NIPPON SHOKUBAI KAGAKU KOGYO Co., Ltd.

Table 1

	Water Absorbing Resin (W.A.R)	cross-linking agent	Amount of wt (mol%)	chain transfer agent	Amoun tof wt (mol%)	Ratio of saline (g/g)	Ratio of human urine (g/g)	Stickines s of gel	Soluble Content (%)	Soluble molecul ar wt (0.1 million)	liquid perme ability (sec.)	durability (6h/12h/ 18h)	Amountof exduction of absorbed liquid (g)
example	W.A.R	TMPT	0.1	SHP	0.008	43	34	G	5.8	9	20	G/G/G	5.8
(1)	(1)												
(2)	(2)	TMPT	0.1	SHP	0.05	54	36	G	13.8	9	30	G/G/A-G	7.7
(3)	(3)	PEGDA	0.2	SHP	0.1	52	34	G	14.6	2	20	G/G/G	8.8
(4)	(4)	PEGDA	0.5	SHP	0.4	43	30	G	15.1	1	20	G/G/G	8.1
(5)	(5)	MBAA	0.06	Thiomalic	0.1	49	36	G	12.1	10	20	G/G/A-G	6.6
(6)	(6)	PEGDA	0.1	-acid	0.02	40	33	G	2.9	7	20	G/G/G	6.4
(7)	(7)	MBAA	0.3	Thiomalic	0.15	41	31	G	3.8	3	10	G/G/G	8.8
(8)	(8)	MBAA	0.15	-acid	0.15	40	28	A-G	9.8	12	40	G/G/A-G	9.8
(9)	(9)			Thiomalic		41	36	G	5.3	8	10or	G/G/G	3.3
(10)	(10)			-acid		51	38	G	13.1	8	less	G/G/G	3.9
(11)	(11)			Thiomalic		50	35	G	14	2	10or	G/G/G	4.4
(12)	(12)			-acid		48	36	G	2.1	1	less	G/G/G	4.1
								(G:good			10or	(G:good	
								A:average			less	A:average	
								P:poor)			10or	P:poor)	
											less		
		(example 1		↑	)								
		(example 2		↑	)								
		(example 3		↑	)								
		(example 4		↑	)								

Comp. example (1)	Comp. W.A.R (1)	TMPT	0.004	SHP	0.008	85	8	P	35.5	93	60or more	P/P/P	18.3
(2)	(2)	TMPT	0.1	NONE	0	36	21	G	5.2	9	50	G/G/G	13.5
(3)	(3)	TMPT	0.05	NONE	0	43	20	A-G	6.2	8	60	G/G/A-G	18.3
(4)	(4)	MBAA	0.5	NONE	0	25	18	G	3	1	40	P/P/P	22.5
(5)	(5)	NONE	0	thiomalic acid	0.1	85	11	P	45.2	100	60or	G/A/G-P	16.3
(6)	(6)					55	19	A	33.1	90	more	A/A-P/P	11.3
(7)	(7)					34	24	G	5	8	60	G/G/A-G	13.1
(8)	(8)	(surface treated product of comparative example 1) (↑ comparative example 2) (↑ comparative example 3)				39	21	G (G:good A:average P:poor)	5.2	8	30 30	(G:good A:average P:poor)	15.1

MBAA : N,N'-methylenebisacrylamide

TMPT : trimethylolpropanetriacrylate

PEGDA : polyethyleneglycoldiacrylate (n=8 or 14)

SHP : sodium hypophosfite1hydrate

⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　平3-179008

⑬Int. Cl.⁵　識別記号　庁内整理番号　㊸公開　平成3年(1991)8月5日

C 08 F 20/06　MBC　7107-4J
2/10　MCJ　8215-4J※
2/38

審査請求　未請求　請求項の数 16　(全13頁)

㊹発明の名称　耐久性の優れた吸水性樹脂の製造方法

㉑特　願　平1-317674
㉒出　願　平1(1989)12月8日

㉗発明者　長砂　欣也　大阪府吹田市西御旅町5番8号　日本触媒化学工業株式会社中央研究所内
㉗発明者　角永　憲資　大阪府吹田市西御旅町5番8号　日本触媒化学工業株式会社中央研究所内
㉗発明者　木村　和正　大阪府吹田市西御旅町5番8号　日本触媒化学工業株式会社中央研究所内
㉗発明者　下村　忠生　大阪府吹田市西御旅町5番8号　日本触媒化学工業株式会社中央研究所内
㉑出願人　日本触媒化学工業株式会社　大阪府大阪市中央区高麗橋4丁目1番1号

最終頁に続く

明　細　書

1．発明の名称

耐久性の優れた吸水性樹脂の製造方法

2．特許請求の範囲

1．水溶性エチレン性不飽和単量体(A)および該単量体(A)に対し、架橋剤(B) 0.005～5モル％および水溶性連鎖移動剤(C) 0.001～1モル％を含有する30重量％～飽和濃度の該単量体(A)水溶液を、水溶液重合させることを特徴とする耐久性の優れた吸水性樹脂(D)の製造方法。

2．水溶性エチレン性不飽和単量体(A)および該単量体(A)に対し、架橋剤(B) 0.005～5モル％および水溶性連鎖移動剤(C) 0.001～1モル％を含有する30重量％～飽和濃度の該単量体(A)水溶液を、水溶液重合させて得た吸水性樹脂(D)の表面近傍を吸水性樹脂(D)中の官能基と反応しうる親水性架橋剤(E)で架橋させることを特徴とする耐久性の優れた吸水性樹脂(F)の製造方法。

3．水溶性連鎖移動剤(C)が次亜燐酸塩である請求項1または2記載の製造方法。

4．架橋剤(B)の使用量が水溶性エチレン性不飽和単量体(A)に対して0.02～1モル％である請求項1または2記載の製造方法。

5．水溶性エチレン性不飽和単量体(A)水溶液の濃度が35重量％～飽和濃度である請求項1または2記載の製造方法。

6．水溶性エチレン性不飽和単量体(A)がアクリル酸およびアクリル酸アルカリ金属塩および／またはアンモニウム塩を少なくとも50重量％含んでなる請求項1または2記載の製造方法。

7．水溶性エチレン性不飽和単量体(A)水溶液を回転撹拌軸を有する反応器内で、水溶液重合させることを特徴とする請求項1または2記載の製造方法。

8．回転撹拌翼を有する反応容器が複数の回転撹拌翼を有してなる請求項7に記載の製造方法。

9．複数の回転撹拌軸を有する反応容器が双腕型ニーダーである請求項8に記載の製造方法。

10．架橋剤(B)の使用量が水溶性エチレン性不飽和単量体(A)に対して0.04～0.4モル％である請求項9に記載の製造方法。

11．吸水性樹脂(D) 100重量部に対して、水0～20重量部および親水性有機溶剤(G) 0～20重量部の存在下、カルボキシル基と反応しうる2個以上の官能基を有する化合物(E-1)及び／または多価金属塩(E-2)からなる群から選ばれた少なくとも1種の親水性架橋剤(E)を0.005～5重量部を混合し、40～250℃で加熱することよりなる請求項2記載の製造方法。

12．親水性架橋剤(E)が化合物(E-1)である請求項11記載の製造方法。

13．化合物(E-1)が多価アルコール化合物、多価グリシジルエーテル化合物、多価オキサゾリン化合物及び多価アミン化合物からなる群から選ばれる1種または2種以上のものである請求項12記載の製造方法。

14．水が吸水性樹脂(D) 100重量部に対して0.5～10重量部の量で用いられてなる請求項11記載の製造方法。

15．親水性有機溶剤(G)が吸水性樹脂(D) 100重量部に対して0～8重量部の量で用いられてなる請求項11記載の製造方法。

16．加熱が90～220℃である請求項11記載の製造方法。

3．発明の詳細な説明

〔産業上の利用分野〕

本発明は耐久性の優れた吸水性樹脂の製造方法に関するものである。更に詳しくは、吸水倍率、吸水速度、膨潤時の耐久性に優れ、膨潤ゲルのベトツキが少なく通液性に優れた吸水性樹脂の製造方法に関するものである。

かかる吸水性樹脂は安価に簡便に製造でき安全性に優れているだけでなく、優れた吸水能を持っているため、生理用品、紙オムツなどの衛生材料として、農園芸、緑化用の保水剤として、更にその広範な吸収性物品の材料として広く使用できる。

〔従来の技術〕

近年、自重の数10倍から数100倍の水を吸収する吸水性樹脂が開発され、紙おむつ、生理用ナプキン等の衛材分野をはじめとして農林業分野、土木分野等に幅広く用いられている。

この様な吸水性樹脂としては、例えばポリアクリル酸部分中和物架橋体（特開昭55-84304号）、澱粉-アクリロニトリルグラフト重合体の加水分解物（特公昭49-43395号）、澱粉-アクリル酸エステル共重合体の中和物（特開昭51-125468号）、酢酸ビニル-アクリル酸エステル共重合体の鹸化物（特開昭52-14689号）、アクリロニトリル共重合体もしくはアクリルアミド共重合体の加水分解物（特公昭53-15959号）またはこれらの架橋体などが知られている。

これら吸水性樹脂に望まれる特性としては、水性液体に接した際の高い吸収倍率や優れた吸水速度、水性液体を含んだ基材から液を吸い上げるための優れた吸引力などが求められる。

しかしながら、吸水性樹脂の用途によっては、特に膨潤ゲルの耐久性、経時安定性が上記特性に加えて必要となってくる。例えば、従来の吸水性樹脂を衛生材料用として紙オムツなどに用いた場合、尿を吸収した吸水性樹脂の膨潤ゲルが経時的に劣化した分解を起こしたり、また農園芸用などの長期間の使用で劣化し分解を起こすことがあった。

これまでに知られている吸水性樹脂の膨潤ゲルの劣化、分解の防止方法としては吸水性樹脂に含酸素還元性無機塩やラジカル連鎖禁止剤などを含有させる方法（特開昭63-118375号、特開昭63-152667号）、酸化剤を含有させる方法（特開昭63-153060号）、硫黄含有還元剤を含有させる方法（特開昭63-272349号）などがある。しかしながら、これらの方法はいずれも吸水性樹脂に劣化防止のための添加剤を加える方法であり、他の添加剤を加えるということは、それら吸水性樹脂が衛生材料などに使用されることを考えると、安全性の面から必ず

しも好ましいものではなかった。

そこで架橋剤量を多く用いて吸水性樹脂の架橋密度を高めることで、ゲル強度を高め耐久性を向上させる方法もあるが、これらの吸水性樹脂は充分な耐久性を持たせるには、高架橋のため吸水倍率が極端に低くなってしまうのが実情であった。このように現在、安全性に優れ、吸水倍率が高く、且つ耐久性に優れた吸水性樹脂は得られていない。

また、上記の耐久性に加えて、オムツなどに組み込んだ際に膨潤ゲルのベトツキや通液性の低下などが問題になることがあった。吸水性樹脂には水溶性となる部分（以下、これを水可溶分と呼ぶ。）が存在し、これら水可溶分のため、吸水後の膨潤ゲルがベトツイたり、オムツなどの吸収物品に組み込んだ際にはこのベトツキのため通液性が低下し、新たな尿が排出された際にモレを起こすことがある。水可溶分量は一般に吸水倍率と正の相関関係にあり、水可溶分低減のためには吸水性樹脂の架橋密度を上げなければならず、その為に可溶分の少ない吸水性樹脂は吸水倍率も低下してしまうのが実情であった。

しかして、この様な吸水性樹脂において架橋剤の配合量を増加すればするほど耐久性が向上することは公知であるが、架橋剤の量が増えればそれだけ吸水倍率が低下するという問題点があった。また吸水性樹脂の製造時に連鎖移動剤を使用することにより吸水倍率を向上させる技術が開示されている。（USP4698404）。しかしこの場合、水や生理食塩水に対する吸水倍率は確かに向上するが人尿に対しては吸水倍率の増加は殆ど認められていない。

〔発明が解決しようとする課題〕

本発明は上記現状に鑑みなされたものである。従って本発明の目的は耐久性の優れた吸水性樹脂の製造方法を提供することにある。

本発明の他の目的は、生理食塩水に対してもまた特に人尿に対しても高い吸水倍率を示し、使い捨てオムツに使用した際に優れた耐久性を示し、且つ該オムツでの戻り量も少なく、ゲルのベトツキ感が少なく通液性に優れた吸水性樹脂の製造方法を提供することにある。

〔課題を解決するための手段及び作用〕

本発明者らは、上記課題を解決すべく鋭意検討した結果、

(1) 特定量の架橋剤(B)と水溶性連鎖移動剤(C)を含有した水溶性エチレン性不飽和単量体(A)水溶液を特定の濃度範囲で水溶液重合することにより、吸水倍率を高く保ちつつ、耐久性が向上し、水可溶分の分子量の低下に伴いゲルのベトツキ感や通液性も改善された良好な吸水性樹脂(D)が生産性よく得られること、

(2) さらに上記(1)の製造方法で得られた吸水性樹脂(D)の表面近傍を親水性架橋剤(E)で架橋させることにより、更に優れた吸水特性の改善効果を示し、高い吸水倍率を保ちつつ、より耐久性、ゲルのベトツキ感や通液性が向上し、吸水特性に優れた吸水性樹脂(F)が得られること、

を見い出し本発明を完成するに至った。

即ち、本発明は、

水溶性エチレン性不飽和単量体(A)および該単量体(A)に対し、架橋剤(B) 0．006～5モル％、水溶性連鎖移動剤(C) 0．001～1モル％を含有する30重量％～飽和濃度の該単量体(A)水溶液を~~分散剤の存在下~~、水溶液重合させることを特徴とする耐久性の優れた吸水性樹脂(D)の製造方法。

並びに、

水溶性エチレン性不飽和単量体(A)および該単量体(A)に対し、架橋剤(B) 0．005～5モル％、水溶性連鎖移動剤(C) 0．001～1モル％を含有する30重量％～飽和濃度の該単量体(A)水溶液を~~分散剤の存在下~~、水溶液重合させて得た吸水性樹脂(D)の表面近傍を吸水性樹脂中の官能基と反応しうる親水性架橋剤(E)で架橋させることを特徴とする耐久性の優れた吸水性樹脂(F)の製造方法。

に関するものである。

本発明をさらに詳しく説明する。

本発明に用いる水溶性エチレン性不飽和単量体

(A)（以下、単量体(A)）としては官能基を有するものであり、例えばアクリル酸、メタクリル酸、マレイン酸、フマール酸、クロトン酸、イタコン酸、ビニルベンゼンスルホン酸、2－（メタ）アクリルアミド－2－メチルプロパンスルホン酸、2－（メタ）アクリロイルエタンスルホン酸、2－（メタ）アクリロイルプロパンスルホン酸、及びそれらのアルカリ金属塩、アンモニウム塩、アクリルアミド、メタクリルアミド、2－ヒドロキシエチル（メタ）アクリレート、メトキシポリエチレングリコール（メタ）アクリレート、N,N-ジメチルアミノエチル（メタ）アクリレート、N,N-ジエチルアミノプロピル（メタ）アクリレート、N,N-ジエチルアミノプロピル（メタ）アクリルアミド、及びそれらの四級塩などを挙げることができ、これらの群から選ばれる少なくとも1種のものが使用できる。

なかでも上記の単量体(A)の内、得られる吸水性樹脂の性能やコストの点からアクリル酸を主成分として用いることが好ましく、その際はアクリル酸及びそのアルカリ金属塩および／またはアンモニウム塩の含有率は単量体(A)の内で50重量％以上とすることが好ましく、更に好ましくは75重量％以上とすることである。

また本発明において耐久性の優れた吸水性樹脂を得るには分子内に2個以上の重合性不飽和基や反応性官能基を有する架橋剤(B)を特定量用いることが必須である。これら架橋剤(B)として例えば、分子内に2個以上の重合性不飽和基を有する化合物として、例えばN，N′－メチレンビスアクリルアミド、（ポリ）エチレングリコールジ（メタ）アクリレート、（ポリ）プロピレングリコールジ（メタ）アクリレート、グリセリントリ（メタ）アクリレート、グリセリンアクリレートメタクリレート、（メタ）アクリル酸多価金属塩、トリメチロールプロパントリ（メタ）アクリレート、トリアリルアミン、トリアリルシアヌレート、トリアリルイソシアヌレート、トリアリルホスフェート等を挙げることができる。また反応性官能基を有するものとしては、例えば、単量体(A)がカルボキシル基を有する場合には、エチレングリコール、ジエチレングリコール、トリエチレングリコール、ポリエチレングリコール、プロピレングリコール、ジプロピレングリコール、ポリプロピレングリコール、グリセリン等の多価アルコール類；（ポリ）エチレングリコールジグリシジルエーテル、グリセロールポリグリシジルエーテル等の多価グリシジル化合物；エチレンジアミン、ポリエチレンイミン等の多価アミン；その他、多価オキサゾリン化合物、ハロエポキシ化合物、多価イソシアネート、多価金属塩等があり、また分子内に重合性不飽和基と反応性官能基を合わせ持つものとしてはグリシジル（メタ）アクリレート、N－メチロール（メタ）アクリルアミド等を例示することが出来る。これらの架橋剤(B)のなかでは、分子内に2個以上の重合性不飽和基を有する化合物を用いることが得られる吸水性樹脂の耐久性や吸水特性の点から特に好ましい。

これら架橋剤(B)の本発明に於ける使用量は、目的とする吸水倍率の吸水性を得るために水溶性連鎖移動剤(C)を用いない他は同一条件で行う場合の架橋剤の使用量に比べて、2～100倍モル、更に好ましくは4～10倍モルである。具体的には、架橋剤(B)の使用量は単量体(A)に対して0．005～5モル％である。これら架橋剤(B)の使用量が0．005モル％未満では得られた吸水性樹脂の吸水倍率は高いものが得られるが、耐久性に劣り且つ水可溶分が多くその分子量も高いためゲルのベトツキ感や通液性に劣ったものとなる。また5モル％を越えて多く使用すると吸水倍率が非常に低いものとなってしまう。また架橋剤の使用量は後述する水溶性連鎖移動剤(C)の使用量にもよるが、好ましくは0．02～1モル％であり、更に好ましくは0．04～0．4モル％であり、更により好ましくは0．08～0．2モル％である。

また上記架橋剤(B)の他に、グラフト重合によって架橋を形成させる方法を併用してもよい。この様な方法として、セルロース、澱粉、ポリビニルアルコール等の親水性高分子の存在下に単量体

(A) 水溶液を重合させ、重合時にグラフト重合に起因する架橋を形成させる方法が挙げられ、これらの水溶性高分子は単量体(A) に対して1～50重量%の範囲で用いるのが好ましい。

本発明は特定量の水溶性連鎖移動剤(C) を用いることが必須である。

本発明の~~吸水性樹脂(D)において~~方法によると、特定量の水溶性連鎖移動剤(C) を選び、且つ通常の製造方法に比べて2～100倍モルと多量の架橋剤を使用し高架橋として重合を行うことで初めて、耐久性が非常に優れ、生理食塩水のみならず人尿に対しても高い吸水倍率を示し、また水可溶分の分子量が低いため、ゲルのベトツキ感や通液性の低下などの悪影響が少ない等と言う、優れた吸水性樹脂が得られる。

本発明に使用する水溶性連鎖移動剤(C) としては、水または水溶性エチレン性不飽和単量体に溶解するものであれば特に制限されず、チオール類、チオール酸類、2級アルコール類、アミン類、次亜燐酸塩類などを挙げることができ、具体的にはメルカプトエタノール、メルカプトプロパノール、ドデシルメルカプタン、チオグリコール酸、チオリンゴ酸、3－メルカプトプロピオン酸、イソプロパノール、次亜燐酸ナトリウム、蟻酸、およびそれらの塩類が使用され、これら群から選ばれる1種または2種以上が用いられるが、その効果から次亜燐酸ナトリウムなどの次亜燐酸塩を用いることが好ましい。

水溶性連鎖移動剤(C) の使用量は水溶性連鎖移動剤の種類や使用量、単量体(A) 水溶液の濃度にもよるが、単量体(A) に対して0．001～1モル%であり、好ましくは0．005～0．3モル%である。この使用量が0．001モル%未満では、本発明~~の~~に用いる架橋剤(B) の使用量では架橋密度が高く吸水倍率が低くなりすぎて好ましくない。また1モル%を越えて多く使用すると水可溶分が増加し、耐久性がかえって低下するので好ましくない。

本発明に用いられる単量体(A) 水溶液の濃度としては30重量%～飽和濃度、より好ましくは35重量%～飽和濃度の範囲である。30重量%未満の濃度では単位反応容積当りの生産性が下がり、また乾燥工程にも時間を要し、生産性が低下して工業的観点から好ましくない。従来の重合方法では生産性向上のため飽和濃度付近で重合を行うと自己架橋などの不要な反応が起こり吸水倍率が低下するため、重合時に使用できる架橋剤(B) の量が限られ、そのため耐久性に乏しい吸水性樹脂しか得られなかった。しかし本発明の方法によれば、水溶性連鎖移動剤(C) の使用量を選ぶことによって自己架橋反応が抑制され、架橋剤(B) の使用量が増やせるので耐久性に優れた高吸水倍率の吸水性樹脂を高濃度で生産性よく製造することができる。

また必要に応じて単量体(A) 水溶液に増粘剤を使用してもよい。この様な増粘剤としては、例えばポリビニルピロリドン、ポリアクリルアミド、メチルセルロース、ヒドロキシエチルセルロース等を挙げることができる。

本発明に於て単量体(A) 水溶液を重合させ吸水性樹脂を得る重合方法としては、公知の重合技術、例えば水溶液重合、逆相懸濁重合、沈殿重合、塊状重合、紫外線や電子線などの活性エネルギーによる重合などの中で、性能面や生産性やコスト面で優れた吸水性樹脂を得る方法として水溶液重合が採用される。水溶液重合を行う方法としては、例えば型枠の中で行う注型重合（特公昭48－42466）、ベルトコンベアー上で重合する方法（特開昭58－49714）、含水ゲル状重合体を細分化できるような撹拌羽根を有するニーダーなどの中で重合する方法（特開昭57－34101）などが例示できる。

この様な水溶液重合が行われる場合、水溶性連鎖移動剤(C) による均一な連鎖移動反応や架橋剤(B) による均一な架橋反応を進行させ、より性能の優れた吸水性樹脂を得るためには、重合熱が均一に除去されることが好ましい。そのためには重合ゲルが一体となる重合法ではなく、重合の開始から終了までの全時間あるいは一部で、好ましくは全時間で反応系の重合ゲルが撹拌され重合熱の

均一な除去がなされることが好ましく、よって重合反応は回転撹拌翼を有する反応容器内で行われることが好ましい。回転撹拌翼を有する反応容器としては、特に制限はないが、重合ゲルに対する撹拌力が大きいものが好ましく、重合の進行に伴い生成する重合ゲルを回転撹拌翼によって剪断力を与える反応機なども例示でき、また撹拌力を大きくするためには回転撹拌翼は複数であることがより好ましい。反応機としては例えば一軸の混練機、一軸の押出機、双腕型ニーダーおよび三軸ニーダーなどが挙げられる。また双腕型ニーダーを用いると、重合ゲルを細かく細分化し重合の全時間にわたり均一に撹拌ができ重合熱の均一な除去を行えるので、より性能の優れた吸水性樹脂が得られるので好ましい。

本発明に於て、水溶液重合に使用されるラジカル重合開始剤としては水溶性であれば特に制限されず、例えば過硫酸カリウム、過硫酸アンモニウム、過硫酸ナトリウム等の過硫酸塩；過酸化水素；t－ブチルハイドロパーオキサイド、クメンハイドロパーオキサイド等のハイドロパーオキサイド；2,2'－アゾビス（2-アミジノプロパン）二塩酸塩等のアゾ化合物；その他、第二セリウム塩、過マンガン酸塩等が挙げられる。中でも得られた吸水性樹脂の性能面や分解生成物の安全性等の点から、過硫酸塩、過酸化水素、アゾ化合物よりなる群から選ばれる1種または2種以上が好ましい。

またラジカル重合開始剤が酸化性ラジカル重合開始剤の場合、還元剤を併用してレドックス系開始剤として用いても良い。用いられる還元剤としては、例えば亜硫酸ナトリウム、亜硫酸水素ナトリウム等の亜硫酸（水素）塩；チオ硫酸ナトリウム等のチオ硫酸塩；亜二チオン酸塩；硫酸第一銅、硫酸第一鉄等の金属塩；ℓ－アスコルビン酸等の有機還元剤；アニリン，モノエタノールアミン等のアミン類が挙げられる。

ラジカル重合開始剤の使用量は広い範囲とすることができるが、通常、単量体(A) に対して0．001～2モル%の範囲とするのが好ましく、更に好ましくは0．01～0．5モル%の範囲である。この使用量が0．001モル%未満では重合時間や誘導期間が長くなり、また残存モノマーも多くなり易く好ましくない。また従来の重合方法では、残存モノマー低減や誘導期間、重合時間の短縮のため、重合開始剤量を増加させると自己架橋などの不要な反応が起こり吸水倍率が低下するため、使用できる開始剤量も限られてきていたが、本発明の方法によれば、かかる欠点は改善され開始剤量は増加させても高性能の吸水性樹脂が得られる。しかし2モル%より多く使用しても、添加量に見合った効果が少ないばかりか、重合反応の制御が困難となってしまうので好ましくない。

本発明で得られる吸水性樹脂は高濃度で重合させその重合熱により乾燥と重合を同時に行っても良いし、重合後の含水率によっては得られた含水ゲルを更に乾燥することによって吸水性樹脂として使用してもよい。乾燥方法としては公知の乾燥方法を用いることができ、例えば有機溶剤中での共沸脱水による方法、強制通風炉、減圧乾燥器、マイクロ波乾燥器、赤外線乾燥器、所定温度に加熱されたベルトまたはドラムドライヤー等を用いる乾燥方法が挙げられる。これらの乾燥方法を用い、重合後の含水ゲルを80℃以上で、より好ましくは80～230℃で乾燥することが好ましい。80℃~~以下~~未満では乾燥に時間がかかり生産性の点から好ましくない。また230℃~~以上では~~を越えると吸水性樹脂の劣化が起こる場合があるので注意を要する。

また以上の様に重合、乾燥して得られた吸水性樹脂は、必要により粉砕およびまたは分級して使用される。

さらに本発明は、前記製造方法によって得られる吸水性樹脂(D) の表面近傍を特定の親水性架橋剤(E) で架橋させた吸水性樹脂(F) の製造方法をも提供する。本発明の前記製造方法によって得られた吸水性樹脂(D) は、~~表面近傍の架橋によって~~従来の吸水性樹脂に比べて著しい吸水特性の改善効果を示し、表面近傍を架橋した吸水性樹脂(F) は表面近傍を架橋する前の吸水性樹脂(D) に比べ、さらに耐久性に優れ吸水特性に優れたものに

なる。

本発明に於て使用される親水性架橋剤(E) としてはカルボキシル基と反応しうる官能基を1分子中に2個以上有する化合物(E-1) 及び／または多価金属塩(E-2) である。例えば吸水性樹脂(D) がカルボキシル基を有する場合には、化合物(E-1) としてはエチレングリコール、ジエチレングリコール、トリエチレングリコール、テトラエチレングリコール、ポリエチレングリコール、1,4-ブタンジオール、1,5-ペンタンジオール、1,6-ヘキサンジオール、ネオペンチルグリコール、プロピレングリコール、グリセリン、ポリグリセリン、トリメチロールプロパン、ペンタエリスリトール、ソルビトール、ポリビニルアルコール等の多価アルコール化合物；エチレングリコールジグリシジルエーテル、ポリエチレングリコールジグリシジルエーテル、グリセロールポリグリシジルエーテル、ジグリセロールポリグリシジルエーテル、ポリグリセロールポリグリシジルエーテル、プロピレングリコールジグリシジルエーテル、ポリプロピレングリコールジグリシジルエーテル等の多価グリシジルエーテル化合物；エチレンジアミン、ジエチレントリアミン、トリエチレンテトラミン、ポリエチレンイミン等の多価アミン化合物；1,2-エチレンビスオキサゾリン、ポリイソプロペニルオキサゾリン等の多価オキサゾリン化合物；エピクロロヒドリンなどのハロエポキシ化合物；その他の多価アジリジン化合物、多価イソシアネート化合物などが挙げられ、多価金属塩(E-2) としては亜鉛、カルシウム、マグネシウム、アルミニウム、鉄、ジルコニウム等の水酸化物及び塩化物などが挙げられる。これらの群より1種または2種以上を用いることが好ましく、中でも化合物(E-1) を必須に用いることが好ましく、特に多価アルコール類、多価グリシジル化合物類、多価アミン類を親水性架橋剤(E) として用いることが表面架橋効果の点から好ましい。また親水性架橋剤(E) として、化合物(E-1) と多価金属塩(E-2) を併用して用いて混合性を向上させても構わない。

本発明に於て使用された親水性架橋剤(E) の量は上記、製造方法によって得られた吸水性樹脂(D) 100重量部に対して、0.005～5重量部、好ましくは0.01～1重量部の範囲の割合であり、この範囲内の量であれば諸特性に優れた表面架橋~~せ~~された吸水性樹脂(F) が得られる。親水性架橋剤(E) の量が5重量部を超える場合、不経済となるばかりか、未反応の親水性架橋剤(E) が得られた吸水性樹脂(F) に残存する可能性がある上に、適正な架橋効果を達成する上で過剰量となり得られる吸水性樹脂(F) の吸水倍率は小さくなり好ましくない。また0.005重量部未満の少ない量では本発明の効果が得られにくい。

本発明に於て、吸水性樹脂(D) と親水性架橋剤(E) とを混合する際、水及び／または親水性有機溶剤(G) を用いてもよい。

本発明に於て、水の使用量は吸水性樹脂(D) 100重量部当り0～20重量部~~未満~~、好ましくは0.5～10重量部の範囲の割合である。

また親水性有機溶剤(G) として例えば、メタノール、エタノール、n－プロパノール、iso－プロパノール、n－ブタノール、iso－ブタノール、t－ブタノール等の低級アルコール類；アセトン、メチルエチルケトン、メチルブチルケトン等のケトン類；ジオキサン、テトラヒドロフラン等のエーテル類；N,N-ジメチルホルムアミド等のアミド類；ジメチルスルホキシド等のスルホキシド類を挙げることができ、その使用量は吸水性樹脂(D) 100重量部に対して0～20重量部、好ましくは0～8重量部の範囲の割合である。

本発明に於て、吸水性樹脂(D) を親水性架橋剤(E) と混合し、吸水性樹脂の表面近傍を架橋する方法としては、以下の様な方法が例示される。

(I) 吸水性樹脂(D) に親水性架橋剤(E) および必要により、水（水蒸気）及び／または親水性有機溶剤(G) の混合液を噴霧、あるいは滴下混合する方法。

または、

(II) 吸水性樹脂(D) を重合不活性な疎水性有機溶剤中に分散・懸濁させ、親水性架橋剤(E) および必要により、水及び／または親水性有機溶剤(G) を撹拌下に添加する方法。

この場合、親水性架橋剤(E) を特定の界面活性剤を用いて、予め疎水性有機溶剤に乳化、懸濁させその乳化液を吸水性樹脂(D) の分散懸濁液中に添加する方法が好ましい。

または、

(III) 吸水性樹脂(D) を水と親水性有機溶剤(G) の混合溶剤中に分散させ、親水性架橋剤(E) を添加する方法。

などが挙げられる。

以上の様にして、本発明の方法によって得られる吸水性樹脂(D) と親水性架橋剤(E) および必要により、水及び／または親水性有機溶剤(G) を混合して得られた混合物を加熱処理するには、通常の加熱器や加熱炉を用いることができる。例えば溝型撹拌乾燥器、回転乾燥器、円盤乾燥器、ねつ和乾燥器、流動層乾燥器、気流乾燥器、赤外線乾燥器、誘電加熱乾燥器などである。又(II) の方法で吸水性樹脂(D) に有機溶剤中で親水性架橋剤(E) を添加した後、有機溶剤中でそのまま加熱し反応させてもよい。

加熱処理温度は用いられる親水性架橋剤(E) の種類などにもよるが、40～250℃が好ましく、より好ましくは90～220℃の範囲である。40℃未満では反応に時間がかかり生産性の低下を起こすのみならず、親水性架橋剤(E) の一部が未反応となり得られた吸水性樹脂(F) に残存する恐れがあり好ましくない。250℃を越える高温では、吸水性樹脂(D) の種類によっては熱劣化が起こる場合があるので注意が必要である。

なお、表面架橋した吸水性樹脂(F) や、表面架橋していない吸水性樹脂(D) を必要により破砕造粒してもよい。

【発明の効果】

本発明により得られる吸水性樹脂は従来の方法では得られなかった、膨潤ゲルの耐久性に優れ、生理食塩水や特に人尿に対しても高吸水倍率で、しかも水可溶分の分子量が低く、膨潤ゲルのベトツキや通液性が大幅に改善された、安全な吸水性樹脂である。本発明の方法によればこの様な優れた吸水性樹脂は、水溶性エチレン性不飽和単量体(A) を特定量の架橋剤(B) 及び特定量の水溶性連鎖移動剤(C) の存在下で水溶液重合を行うだけで簡便に製造でき、更に得られた吸水性樹脂(D) の表面近傍を特定の親水性架橋剤(E) で架橋させ、吸水速度や耐久性の格段に向上された吸水性樹脂(F) が得られる。かかる吸水性樹脂(D) および(F) は、安価に製造でき従来にない優れた吸水特性を有しているため、衛生材料、食品用、土木、農業などの分野に幅広く利用できる。

この様に本発明の製造方法により得られた吸水性樹脂~~及びその製造方法~~は、

(1) 従来、高吸水倍率の吸水性樹脂を得るために架橋剤量を減らして重合を行っていたため、膨潤ゲルの耐久性が乏しかったが、本発明の方法では多くの架橋剤を用いても、高吸水倍率なため、膨潤ゲルが優れた耐久性を示す。

(2) 従来の吸水性樹脂では得られなかった、人尿に対する高い吸水倍率を示す。

(3) 用いる単量体を飽和濃度近くの高い濃度で重合させても、自己架橋など不要な反応が抑えられた高性能の吸水性樹脂が得られる為、高濃度で重合が可能で高い生産性で製造ができる。

(4) 本発明の吸水性樹脂は高い吸水倍率は示すが、付随する水可溶分はその分子量が低いため、水可溶分による膨潤ゲルのベトツキや通液性の低下などの悪影響を及ぼさない。

(5) 表面近傍を架橋することで、従来の吸水性樹脂の表面架橋で得られなかった吸水特性の改善効果を示し、更に優れた耐久性や吸水速度を示す。

(6) 従来、残存モノマー低減や誘導期間、重合時間の短縮のため重合開始剤量を増加させると、自己架橋などの不要な反応が起こり高吸水倍率のものが得られなかったが、重合開始剤量を増やしても高吸水率のものが得られ低い残存モノマー量となる。

等の優れた長所を有するものである。

（実施例）

以下、実施例により本発明を説明するが、本発明の範囲はこれらの実施例にのみ限定されるものではない。尚、実施例に記載の吸水性樹脂の諸物性は下記の試験方法によって測定した値を示す。また、部は重量部を示す。

(1) 生理食塩水の吸水倍率

吸水性樹脂1．0gを150mlの0．9重量％塩化ナトリウム水溶液中の入ったビーカーに浸漬し、ゆっくりマグネチックスターラーで攪拌した。6時間後に膨潤ゲルを金網で濾過し、十分に水切りをした後の膨潤ゲルの重さを測定し、以下の式で吸水倍率を算出した。

$$\text{吸水倍率}(g/g)=\frac{\text{膨潤ゲルの重量}}{\text{吸水性樹脂の重量}}$$

(2) 人尿の吸水倍率

(1) の生理食塩水に代えて、成人男子10人からサンプリングした人尿を用いる以外は同様に行い、人尿での吸水倍率を測定した。

(3) 水可溶分

吸水性樹脂0．5gを1000mlの脱イオン水中に分散し、12時間後、濾紙で濾過し、濾液中の固形分を測定して次式に従って水可溶分を求めた。

$$\text{水可溶分}(\%)=\frac{\text{濾液の重量}(g)\cdot\text{濾液の固形分}(\%)}{0.5\,(g)}$$

(4) 水可溶分の分子量

分子量が既知の種々のポリアクリル酸ナトリウムを標準にして、ゲルパーミエーションクロマトグラフィーによって、(3) の方法でサンプリングした水可溶分の分子量を求めた。

(5) 膨潤ゲルの耐久性

不織布、綿状パルプ、吸水紙および防水フィルムからなる市販の子供用オムツ（重量72g）を半分に切り、ポリマー2．5gを綿状パルプと吸水紙の間に均一に散布し、成人の人尿120mlを加えて37℃に放置し、6時間、12時間、18時間後にオムツを開いて中の膨潤ゲルの様子を観察した。劣化状態の判定は、○～△～×の3段階評価とした。

○：膨潤ゲルの形状が保持されている。

△：一部、膨潤ゲルの形状が崩れている。

×：膨潤ゲルの形状が崩れ、ドロドロの流動状となっている。

(6) もどり量

上記膨潤ゲルの耐久性試験に用いた18時間後の子供用オムツの不織布の上に2つ折りにした23cm＊23cmのペーパータオルを10枚かぶせ、40g/cm² の圧力を1分間かけてペーパータオルに戻ってきた尿の量を測定した。

(7) 膨潤ゲルのベトツキ

(1) で吸水倍率を測定した後の膨潤ゲルのベトツキ（ドライ感）を手触りにて測定した。ドライ感の判定は、○～△～×の3段階評価とした。

○：膨潤ゲルはかなりサラサラしてドライ感がある。

△：一部、膨潤ゲルがベトツク。

×：膨潤ゲルがベトツキ、手がヌベヌベしている。

(8) 膨潤ゲルの通液性

第1図に示すように内径63mmのシャーレ1に吸水性樹脂1．0gを入れ、人尿10mlを注ぎ膨潤ゲル2を得る。膨潤ゲル2の上に直径63mmのペーパータオル3を置き、更に第1図に示すように、中央に突出した筒状部を有する円板状のアクリル樹脂製試験器4を置く。1時間室温に放置した後、人尿6mlを注入口5より注ぎ、人尿が全てポリマー中に吸収されるまでの時間を測定し、それをもって、膨潤ゲルの通液性とする。

（実施例1）

アクリル酸414g及びアクリル酸ナトリウムの37重量％水溶液4380g、および架橋剤(B) としてトリメチロールプロパントリアクリレート6．815g（対単量体(A) 0．1モル％）、水溶性連鎖移動剤(C) として次亜燐酸ナトリウム1水和物0．195g（対単量体(A) 0．008モル％）、イオン交換水670gを用いて濃度37％、中和率75％の単量体水溶液を得た後、

窒素ガスを吹き込んで溶存酸素を追い出した。

内容積10ℓのシグマ型羽根を2本有するジャケット付きステンレス製双腕型ねっか機（ニーダー）に蓋をつけ、この反応器に上記の単量体(A) 水溶液を送入し、窒素ガスを吹き込んで反応系内を窒素置換した。ついで2本のシグマ型羽根を回転させると共に、ジャケットに35℃の温水を通じて加熱しながら重合開始剤として過硫酸アンモニウム2．62gと亜硫酸水素ナトリウム0．12gを添加することにより重合を開始させた。重合ピーク時に含水ゲル重合体は約5mmの径に細分化されており、更に攪拌を続け重合を開始して60分後に蓋を外し、ゲルを取り出した。得られた含水ゲル状重合体の細粒化物を50メッシュの金網上に広げ、170℃の温度で50分間熱風乾燥した。この乾燥物をハンマー型粉砕機で粉砕し、20メッシュ金網でふるい分けして20メッシュ通過物の吸水性樹脂(1) を得た。

この吸水性樹脂(1) の諸物性を ~~を同様に~~ 評価し、結果を第1表に示す。

（実施例2）

実施例1に於て、用いられる水溶性連鎖移動剤(C) 次亜燐酸ナトリウム1水和物の使用量を1．219g（対単量体(A) 0．05モル％）とする以外は同様に行い、吸水性樹脂(2) を得た。

この吸水性樹脂(2) を同様に評価し、結果を第1表に示す。

（実施例3）

実施例1に於て、用いられる架橋剤(B) をポリエチレングリコールジアクリレート（n＝8 ；エチレンオキシド平均単位数）21．988g（対単量体0．2モル％）とし、かつ水溶性連鎖移動剤(C) 次亜燐酸ナトリウム1水和物の使用量を2．44g（対単量体(A) 0．1モル％）とする以外は同様に行い、吸水性樹脂(3) を得た。

この吸水性樹脂(3) を同様に評価し、結果を第1表に示す。

（実施例4）

実施例1に於て、用いられる架橋剤(B) ポリエチレングリコールジアクリレート（n＝8）を54．97g（対単量体0．5モル％）とし、かつ水溶性連鎖移動剤(C) 次亜燐酸ナトリウム1水和物の使用量を9．76g（対単量体(A) 0．4モル％）とする以外は同様に行い、吸水性樹脂(4) を得た。

この吸水性樹脂(4) を同様に評価し、結果を第1表に示す。

（実施例5）

実施例1に於て、用いられる架橋剤(B) をN，N'－メチレンビスアクリルアミド2．152g（対単量体(A) 0．06モル％）とし、かつ水溶性連鎖移動剤(C) をチオリンゴ酸3．45g（対単量体(A) 0．1モル％）とする以外は同様に行い、吸水性樹脂(5) を得た。

この吸水性樹脂(5) を同様に評価し、結果を第1表に示す。

（実施例6）

実施例1に於て、用いられるイオン交換水の量を50gに変更し、単量体(A) 水溶液の濃度を42％とし、用いられる架橋剤(B) をポリエチレングリコールジアクリレート（n＝14）17．07g（対単量体(A) 0．1モル％）とし、かつ水溶性連鎖移動剤(C) チオリンゴ酸の使用量を0．69g（対単量体(A) 0．02モル％）とする以外、同様に行い、吸水性樹脂(6) を得た。

この吸水性樹脂(6) を同様に評価し、結果を第1表に示す。

（実施例7）

40gのトウモロコシ澱粉及び600gのイオン交換水を攪拌棒と窒素ガス吹き込み管と温度計を備えた反応容器内に仕込み、55℃で1時間攪拌後、30℃に冷却した。この澱粉水溶液にアクリル酸300g、架橋剤(B) としてN，N'－メチレンビスアクリルアミド1．92g（対単量体(A) 0．3モル％）、水溶性連鎖移動剤(C) としてチオリンゴ酸0．94g（対単量体(A) 0．15モル％）を溶解させ、濃度33％、中和率0％の単量体水溶液を得た。

この単量体水溶液を35℃として、重合開始剤として過硫酸ナトリウム0．20g、ℓ－アスコ

ルビン酸0．04gを加えて3時間、攪拌しながら重合せしめた。得られた含水ゲル状重合物に、30重量%の苛性ソーダ水溶液を389g加え、中和率70%とし、更に実施例1と同様に乾燥粉砕し吸水性樹脂(7)を得た。

この吸水性樹脂(7)を同様に評価し、結果を第1表に示す。

（実施例8）

アクリル酸72gに脱イオン水22．2gを加え、更にこれを中和剤として純度85%の水酸化カリウム49．5gおよび架橋剤(B)としてN，N'－メチレンビスアクリルアミド0．1g（対単量体(A) 0．065モル%）、水溶性連鎖移動剤(C)としてチオリンゴ酸0．225g（対単量体(A) 0．15モル%）を順次添加し、濃度70%、中和率75%の単量体水溶液を調整した。

この単量体水溶液を70℃に保温し、約5mmの厚みに窒素気流下に保った後、更に過硫酸アンモニウム0．1gおよび亜硫酸水素ナトリウム0．02gを添加し重合を行った。重合は即座に開始し、10分後に殆ど乾燥した重合ゲルを取り出し、更に実施例1と同様に乾燥粉砕し吸水性樹脂(8)を得た。

この吸水性樹脂(8)を同様に評価し、結果を第1表に示す。

（実施例9）

実施例1で得られた吸水性樹脂(5) 100部にエチレングリコールジグリシジルエーテル0．1部、水5部、イソプロピルアルコール1部を混合し、得られた混合物を乾燥機中に100℃、30分間加熱処理を行い、吸水性樹脂(9)を得た。

この様にして得られた吸水性樹脂(9)の分析結果を第1表に示す。

（実施例10）

実施例2で得られた吸水性樹脂(2) 100部に、グリセリン1部、水6部、アセトン1部を加え、ジャケットを熱媒で230℃に加熱したブレンダーに投入し、混合と加熱処理を行い吸水性樹脂(10)を得た。

この様にして得られた吸水性樹脂(10)の分析結果を第1表に示す。

（実施例11）

実施例3で得られた吸水性樹脂(3) 100部にエチレングリコールジグリシジルエーテル0．1部、水3部、メタノール8部からなる処理溶液を混合した。得られた混合物を乾燥機中、130℃で1時間加熱処理することにより吸水性樹脂(11)を得た。

この様にして得られた吸水性樹脂(11)の分析結果を第1表に示す。

（実施例12）

実施例4で得られた吸水性樹脂(4) 100部に硫酸アルミニウム1部、グリセリン1部、水8部からなる処理水溶液10部を混合した。得られた混合物を200℃で30分間加熱処理を行い吸水性樹脂(12)を得た。

この様にして得られた吸水性樹脂(12)の分析結果を第1表に示す。

（比較例1）

実施例1において、架橋剤(B)の使用量を0．273g（対単量体(A) 0．004モル%）とする以外は同様に行い、比較吸水性樹脂(1)を得た。

この様にして得られた比較吸水性樹脂(1)の分析結果を第1表に示す。

（比較例2）

実施例1において、水溶性連鎖移動剤(C)次亜燐酸ナトリウム1水和物を添加しない以外は同様に行い、比較吸水性樹脂(2)を得た。

この様にして得られた比較吸水性樹脂(2)の分析結果を第1表に示す。

（比較例3）

実施例1において、水溶性連鎖移動剤(C)次亜燐酸ナトリウム1水和物を添加せず、架橋剤(B)の使用量を3．41g（対単量体(A) 0．05モル%）とする以外は同様に行い、比較吸水性樹脂(3)を得た。

この様にして得られた比較吸水性樹脂(3)の分析結果を第1表に示す。

（比較例4）

実施例1において、水溶性連鎖移動剤(C)次亜燐酸ナトリウム1水和物を添加せず、架橋剤(B)をN，N'－メチレンビスアクリルアミド17．73g（対単量体(A) 0．5モル%）とする以外は同様に行い、比較吸水性樹脂(4)を得た。

この様にして得られた比較吸水性樹脂(4)の分析結果を第1表に示す。

（比較例5）

実施例7において、架橋剤(B)を添加しない以外は同様に行い、比較吸水性樹脂(5)を得た。

この様にして得られた比較吸水性樹脂(5)の分析結果を第1表に示す。

（比較例6～8）

比較例1～3で得られた比較吸水性樹脂(1)～(3)をそれぞれ、実施例9と同様の操作を行い、比較吸水性樹脂(6)～(8)を得た。

この様にして得られた比較吸水性樹脂(6)～(8)の分析結果を第1表に示す。

第1表

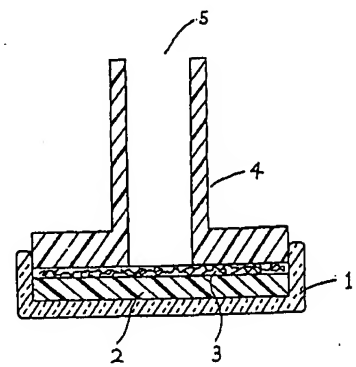
	吸水性樹脂	架橋剤	同量 (モル%)	連鎖移動剤	同量 (モル%)	倍率 生食 (g/g)	倍率 人尿 (g/g)	ゲルのベトツキ	可溶分 (%)	可溶分分子量 (万)	通液性 (分)	耐久性 6h/12h/18h	戻り量 (g)
実施例(1)	吸水性樹脂(1)	TMPT	0.1	SHP	0.008	43	34	○	5.8	9	20	○/○/○	5.6
(2)	(2)	TMPT	0.1	SHP	0.05	54	36	○	13.1	9	30	○/○/△～○	7.1
(3)	(3)	PEGDA	0.2	SHP	0.1	52	34	○	14.6	2	20	○/○/○	6.8
(4)	(4)	PEGDA	0.5	SHP	0.4	43	30	○	15.1	1	20	○/○/○	8.1
(5)	(5)	MBAA	0.06	チオリンゴ酸	0.1	49	38	○	12.1	10	20	○/○/△～○	6.6
(6)	(6)	PEGDA	0.1	チオリンゴ酸	0.02	40	33	○	2.9	7	20	○/○/○	5.4
(7)	(7)	MBAA	0.3	チオリンゴ酸	0.15	41	31	○	3.8	3	10	○/○/○	6.8
(8)	(8)	MBAA	0.15	チオリンゴ酸	0.15	40	28	△～○	9.8	12	40	○/○/△～○	3.8
(9)	(9)	(実施例1		〃	)	41	36	○	5.3	8	10以下	○/○/○	3.3
(10)	(10)	(実施例2		〃	)	51	38	○	13.1	8	10以下	○/○/○	3.9
(11)	(11)	(実施例3		〃	)	50	35	○	14	2	10以下	○/○/○	4.4
(12)	(12)	(実施例4		〃	)	48	38	○	2.1	1	10以下	○/○/○	4.1
比較例(1)	比較吸水性樹脂(1)	TMPT	0.004	SHP	0.008	45	8	×	35.5	93	60以上	×/×/×	18.3
(2)	(2)	TMPT	0.1	なし	0	36	21	○	5.2	8	50	○/○/○	13.5
(3)	(3)	TMPT	0.05	なし	0	43	20	△～○	6.2	8	60以上	○/○/△～○	18.3
(4)	(4)	MBAA	0.5	なし	0	25	18	○	3	1	40	○/○/○	22.5
(5)	(5)	なし	0	チオリンゴ酸	0.1	45	11	×	45.2	100	60以上	×/×/×	16.3
(6)	(6)	(比較例1の表面処理品			)	65	19	△	33.1	90	60	○/△/○～×	11.3
(7)	(7)	(比較例2		〃	)	34	24	○	5	8	30	△/△～×/×	13.1
(8)	(8)	(比較例3		〃	)	39	21	○	5.2	8	30	○/○/△～○	15.1

MBAA　：N，N'－メチレンビスアクリルアミド
TMPT　：トリメチロールプロパントリアクリレート
PEGDA　：ポリエチレングリコールジアクリレート（n＝8，または14）
SHP　：次亜燐酸ナトリウム1水和物

4．図面の簡単な説明

第1図は膨潤ゲルの透液性試験器具を示したものである。

1……　シャーレ
2……　膨潤ゲル
3……　ペーパータオル
4……　アクリル樹脂製試験筒
5……　注入口



第1図

特許出願人　日本触媒化学工業株式会社

第1頁の続き

⑤Int. Cl.⁵		識別記号	庁内整理番号
C 08 F	8/14	MGL	8016-4J
	8/32	MHL	8016-4J